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The development of new thermosetting polymers from bio-based natural feedstocks has recently received increasing attention due to the desire to replace substances that are not only dependent on petroleum supplies, but, as in the case of Bisphenol A, have been the subject of scrutiny due to possible health and safety concerns.1 Although much effort is currently focused on finding replacements for the most commonly used thermosetting resins, in applications such as aerospace where product qualification activities incur significant time and cost, an alternative strategy has been to investigate bio-based products with superior performance, so that the required qualification activities result in a higher payoff. Although the predominant assumption among chemists and engineers is that there will likely be some loss in properties when substituting a bio-based thermosetting polymer for a petroleum-based one, there are a number of natural products that could potentially be converted into resins with superior properties, due to the presence of chemical structures in the repeat unit for these products that are known to provide enhanced properties in thermosetting resins.

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HIGH-PERFORMANCE BIO-BASED CYANATE ESTER RESINS WITH LOW MOISTURE UPTAKE

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Introduction

The development of new thermosetting polymers from bio-based natural feedstocks has recently received increasing attention due to the desire to replace substances that are not only dependent on petroleum supplies, but, as in the case of Bisphenol A, have been the subject of scrutiny due to possible health and safety concerns.[1] Although much effort is currently focused on finding replacements for the most commonly used thermosetting resins, in applications such as aerospace where product qualification activities incur significant time and cost, an alternative strategy has been to investigate bio-based products with superior performance, so that the required qualification activities result in a higher payoff. Although the predominant assumption among chemists and engineers is that there will likely be some loss in properties when substituting a bio-based thermosetting polymer for a petroleum-based one, there are a number of natural products that could potentially be converted into resins with superior properties, due to the presence of chemical structures in the repeat unit for these products that are known to provide enhanced properties in thermosetting resins.

As an example, the Naval Air Warfare Center, Weapons Division has recently supplied cyanate ester monomers based on the natural product *trans*-anethole, which is found at a natural occurrence of >90% in the essential oil of star anise (*Illicium verum*), an evergreen native to portions of China and Vietnam.[2] The structure of the compound (shown in **Figure 1**) enables the production of cyanate esters (also shown in **Figure 1**) that combine high aromaticity with a variable degree of rigidity. In particular, the cross-link density of cured polycyanurate networks based on these monomers was expected to be significantly lower than those based on Bisphenol A or its close chemical analogues, and recent work by us has shown that a lower density of cyanurate groups can lead to lower moisture uptake.[3] The properties of these resins were thus investigated to determine the available combination of glass transition temperature and moisture uptake, and compared to the more traditional cyanurate resins.

Experimental

Materials. The synthesis of the cyanate esters (CE-1) and (CE-2) shown in **Figure 1** from anethole was performed at the Naval Air Warfare Center, Weapons Division and will be covered in a future publication. For comparison, the dicyanate ester of Bisphenol A, that is 2,2'-bis(4-cyanato)propane, or "BADCy", was received from Lonza.

Sample Preparation. No added catalyst was used in the curing of samples. Silicone molds (R2364A, Silpak Inc., mixed at 10:1 by weight with R2364B platinum-based curing agent and cured overnight at room temperature, followed by post-cure at 150 °C for 1 hour) were prepared by de-gassing for 60 minutes at 95 °C and 300 mm Hg. Cyanate ester monomers were de-gassed for 30 minutes at 95 °C and 300 mm Hg, then poured into the prepared mold. The open mold and sample were then placed under flowing nitrogen and cured. Cure was accomplished by heating to 150 °C for 1 hour, followed by 24 hrs at 210 °C. All curing operations took place under nitrogen, and all schedules produced void-free samples 1-3 mm thick. The temperature ramp rate during cure was 5 °C/min.

Test Procedures. Density was determined by placing selected samples in aqueous solutions of $CaCl_2$ (added as the dihydrate) and varying the $CaCl_2$ concentration until neutral buoyancy was observed on bubble-free samples over a period of several minutes. The density of the neutrally buoyant solution was determined by placing 10.00 mL in a volumetric flask (calibrated with deionized water at 20 °C) and weighing, and checked against the predicted density of the solution at ambient temperature based on the known concentration of $CaCl_2$. The van der Waals volume per repeat unit of the samples was calculated in two steps. First, the method of Bicerano[4] was used to calculate the van der Waals volume of the monomer. For monomers, this method produces results that are nearly identical to other techniques.[5] The Bicerano method, however, does not account for the effects of cure well (largely because there is no defined correction for imine groups). Thus, to account for cure, the change in van der Waals volume on cyclotrimerization derived by Georjon and Galy[5] was applied to the value for the monomer. The resultant van der Waals volume was divided by the computed molar volume (assuming complete cure) to derive a packing fraction. Note that the actual packing fraction will differ slightly from that reported due to conversions being slightly less than unity. Water uptake was determined by placing unused samples in approximately 300 mL of deionized water at 85 °C for 96 hours, with sample dimensions and weight measured before and after exposure.
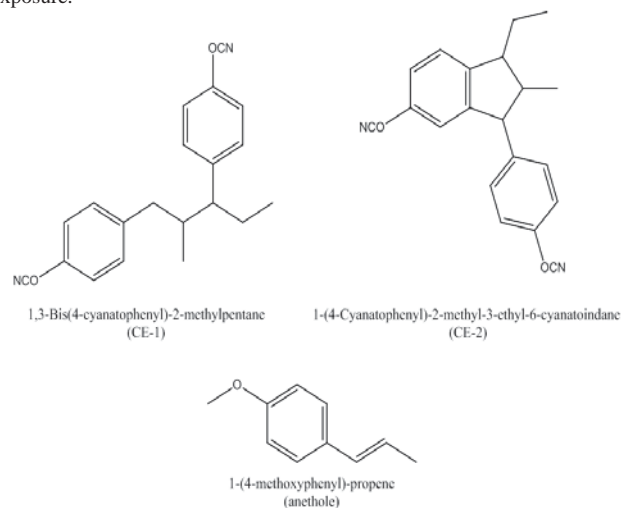

Figure 1. Chemical structures of anethole and the cyanate esters derived from it

Dynamic thermomechanical analysis was performed under oscillatory compression to determine the glass transition temperatures of samples before and after exposure to boiling water. The dynamic TMA technique is similar to traditional DMTA, but provides only a relative measure of stiffness as opposed to an absolute modulus. A detailed description of the dynamic TMA experiments is provided elsewhere.[6] In order to avoid *in-situ* cure, heating rates were 50 °C/min for all samples. This rapid heating rate necessitated the use of the final heating and cooling runs to/from 350 °C in the dynamic TMA for calculation of thermal lag, rather than the initial temperature cycling.

Results and Discussion

The density, packing fraction, dry glass transition temperature (T_g) and water uptake of CE-1 and CE-2 are compared to BADCy in **Table 1**. The packing fractions for all three compounds were similar, with that of CE-1 being modestly higher than CE-2, and that of CE-2 modestly higher than BADCy. Moreover, the cyanurate densities were calculated based on the density and molar volume (assuming full cure) and differed by less than 3% for CE-1 and CE-2 (both near 2.4 mmol cyanurate / cc but significantly lower than BADCy at about 2.9 mmol cyanurate / cc). Since rigidity has been shown to make obtaining complete cure of cyanurate networks more difficult,[7,8] the extent of cure for CE-2 is likely a few per cent less than CE-1, thus in reality the cyanurate densities are likely to be almost identical.

The effect of rigidity on glass transition temperature of the sample is clearly apparent from the data in **Table 1** as well. Interestingly, the more rigid CE-2 achieved an equivalent "as-cured" T_g to BADCy, despite the much higher density of cross-links in BADCy. The effectiveness of rigid linkages in dicyanates at raising the glass transition temperature of the network has been demonstrated previously.[9] Although CE-1 did achieve a lower moisture uptake compared to BADCy, CE-2 did not. Thus, to date, the anethole-derived networks have produced both lower moisture uptake and equivalent glass transition temperatures compared to BADCy, but not in the same

network. It should be noted that both T_g and moisture uptake are strongly dependent on the extent of cure in the sample.

Since moisture uptake was expected to increase with increasing cyanurate density, the higher moisture uptake of CE-2 compared with CE-1 and BADCy might at first seem surprising. However, for cyanurate networks cured below the glass transition temperature, the moisture uptake has been shown to increase significantly with increasing cure near full conversion.[3,5] This effect occurs because below T_g, the network is unable to shrink in response to the loss of van der Waals volume that accompanies cyclotrimerization, resulting not only in increased free volume, but apparently in the creation of free volume with size and location characteristics (near more polar groups in the network) that strongly favor moisture uptake. For CE-1, the final cure temperature is very near the network T_g, thus the formation of this type of free volume never takes place, resulting a much lower overall moisture uptake. This same effect would have lowered the packing fraction in CE-2 and BADCy relative to CE-1, however the modest observed difference in packing fraction among these compounds likely reflects both the aforementioned effect as well as the effect of the differing chemical structures. Note also that while the packing fraction of CE-2 was higher than BADCy, the moisture uptake was higher in CE-2.

These results show that by itself, packing fraction does not provide a complete explanation for moisture uptake, rather the specific characteristics of the free volume in the sample must be taken into account. Although such a task might seem difficult experimentally, in fact, a simple comparison of the cure protocol with the expected dependence of T_g on cure (which may be obtained via the diBenedetto equation)[10] as well as the kinetics of cure will be sufficient to describe the development of free volume that is favorable to moisture uptake, and studies of the dependence of density on the degree of cure can be undertaken to quantify this effect. With such data in hand, it may be possible to design a single network (using either CE-2 or a blend of CE-1 and CE-2) that provides both a higher glass transition temperature and lower moisture uptake compared to BADCy. These studies will be the subject of future work.

Conclusions

An examination of the physical characteristics of cyanurate networks formed from bio-based cyanate esters synthesized from the natural product anethole showed that both equivalently high glass transition temperatures and lower moisture uptake compared to commercial materials could be achieved, though, for the non-optimal cure schedules studied, not in the same network. The most important factor in moisture uptake appeared to be the relation between the cure schedule and the glass transition temperature of the developing network. By optimizing these parameters, it may be possible to produce networks that exhibit both a higher glass transition temperature as well as lower moisture uptake compared to commercial materials.

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Table 1. Physical characteristics of cyanurate networks (uncatalyzed)

Name	"As cured" density (g/cc)	Approx. packing fraction	"As cured" T_g (°C)	Moisture Uptake
CE-1	1.154	0.631	213	1.14%
CE-2	1.176	0.626	279	1.66%
BADCy	1.208	0.620	275	1.34%